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TiO_2: Manufacture of Titanium Dioxide

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5: Manufacture of titanium dioxide

Titanium dioxide has many uses. It is now the common white pigment in paints after the use of lead oxide was banned some years ago. It is also used as a pigment in printing inks, plastics, cosmetics, soap, toothpaste and food. Titanium dioxide is good choice as a pigment as it is chemically resistant and non-toxic.

Even though titanium dioxide is fairly abundant, it is often found in low concentrations in ores.

To make it worthwhile for mining, it needs to be found in purer form and higher concentration. The production of pure titanium dioxide involves several stages and is demanding in terms of chemical reagents and energy.

Pure titanium dioxide exists in different forms and the forms anatase and rutile have photocatalytic properties (see sheet 3: A new kind of water treatment – What is solar disinfection and how does it work?). Apart from water and air purification, these properties have found use in the production of self-cleaning glass and a new type of solar cell called 'Grätzel cell'.

Titanium dioxide mining

The production costs for titanium dioxide are relatively high. However, compared to other minerals, the titanium dioxide market produces relatively high profits, because there is a rising demand and a constant supply. In 2003, the biggest producers of titanium dioxide were Australia, South Africa and Canada.

The world's largest rutile mine, the Sierra Rutile Mine, is in Sierra Leone. The operation covers an area of 580 km^2 and is valued at over 3 billion dollars. In 1995, this mine alone produced 25% of the world's rutile production.

How is pure titanium dioxide manufactured?

Once the titanium containing ores have been mined, they need to be converted into pure titanium oxide. The two main production methods are the sulfate process and the chloride process.

Sulphate Process

In the sulfate process, ilmenite ($FeTiO_3$), a common iron/titanium oxide material, is used. It is treated with concentrated sulfuric acid (H_2SO_4) and the titanium oxygen sulfate ($TiOSO_4$) is selectively extracted and converted into titanium dioxide.

1. Ilmenite is treated (digested) with a 60% excess of concentrated sulfuric acid at a temperature around 100 °C. The following reaction takes place:

$$FeTiO_3 + 2H_2SO_4 \rightarrow FeSO_4 + TiOSO_4 + 2H_2O$$

2. In the next stage, the waste product iron(II)sulfate is removed. As $FeSO_4$ is not very soluble at low temperatures, the solution is cooled to around 15 °C and $FeSO_4$ crystallises out. It can then be removed by filtration.

The remaining aqueous digestion products are heated to around 110 °C in order to hydrolyse the titanium oxygen sulphate.

$$TiOSO_4 + (n+1)H_2O \rightarrow TiO_2{\bullet}nH_2O + H_2SO_4$$

The hydrolysis stage of the process produces sulfuric acid waste and a precipitate gel containing hydrated titanium dioxide.

3. In the last stage, the hydrated titanium dioxide is heated in large rotary kilns to drive off the water and produce crystals of anatase or rutile (2 forms of titanium dioxide).

$$TiO_2{\bullet}nH_2O \rightarrow TiO_2 + nH_2O$$

Water is removed at temperatures between 200–300 °C. Seed crystals are added to start the crystallisation process. Depending on the final heating temperature (800−850 °C or 900−930 °C), either anatase or rutile is formed, respectively.

The sulfate process requires the use of very large quantities of sulfuric acid and produces copious amounts of acidic waste. This acidic waste could cause significant damage to the environment, if not disposed of responsibly.

Chloride Process

1. The chloride process requires purer ore or rutile which is a much rarer. The raw material must contain at least 70% rutile. Titanium dioxide is reduced with carbon and then oxidised again with chlorine.

$$TiO_2 + C \rightarrow Ti + CO_2$$

$$Ti + 2Cl_2 \rightarrow TiCl_4$$

2. Liquid $TiCl_4$ is distilled off and converted back into TiO_2 in a pure oxygen flame or in plasma at temperatures of 1200–1700 °C. The majority of chlorine is recovered.

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2$$

This process also uses a large amount of hazardous chemicals and substantial quantities of energy. Apart from solid or liquid waste of unreacted minerals or different chlorine compounds, the chloride process can produce gaseous particulates, chlorine and sulphur dioxide emissions. The chloride process has been favoured on financial and environmental grounds since the early 1990s.

Rutile, Anatase and Brookite

The three common phases of titanium dioxide are rutile, anatase and brookite. Rutile is the most stable form of titanium dioxide. Anatase and brookite are stable at normal temperatures but slowly convert to rutile upon heating to temperatures above 550 and 750 °C, respectively.

The smallest unit of a crystal is called a unit cell. A crystal can be formed by repeating the unit cell. All three forms of titanium dioxide have six co-ordinated titanium atoms in their unit cells.

Both the more stable rutile (Figure 1(a)) and the metastable anatase (Figure 1(b)) structures are tetragonal. The anatase unit cell is more elongated. In the rutile form, the atoms occupy the least space. This makes the rutile form the most stable at higher temperatures.

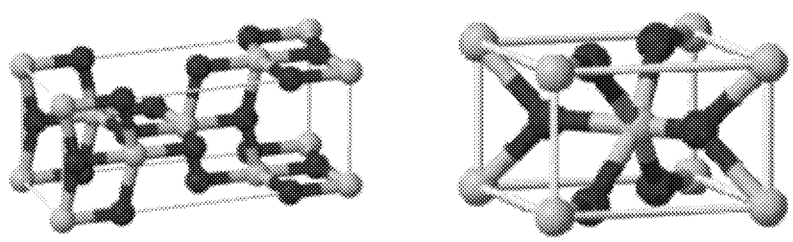

Figure 1 Unit cells of (a) anatase (www.chemtube3d.com/solidstate/_anatase(final).htm) and (b) rutile (www.chemtube3d.com/solidstate/_rutile(final).htm). The titanium atoms are shown in grey, the oxygen atoms in red.

Producing nano-structured titanium dioxide

Pure $TiCl_4$ liquid is vaporised by heating and mixed with air and hydrogen. The gases are heated in a burner at high temperatures between 1000 and 2400 °C, where they react.

Titanium chloride is converted to titanium oxide and hydrogen gas combines with chloride ions to form HCl.

$$TiCl_4 + 2H_2 + O_2 \rightarrow TiO_2 + 4HCl$$

The titanium dioxide formed is pure and contains nano-sized particles with a size (diameter) of approximately 21 nm. If the particles are suspended in a liquid or applied as a coating on glass, particles of this size are not visible to the human eye and the liquid or glass appears transparent.

By comparison, titanium dioxide used as white pigment has a particle size of about 300 nm.

Properties of TiO_2 P25

Manufacturers produce nano-structured titanium dioxide with good photocatalytic properties. TiO_2 P25 (with particle size around 25 nm) is a fine white powder with hydrophilic character meaning it interacts well with water because the TiO_2 surface is coated with hydroxyl groups which can form hydrogen bonds with water molecules.

In the powder, particles with a diameter of approximately 21 nm join together and form aggregates (where a number of primary particles are loosely bound together). The density of TiO_2 P25 is about 4 g cm^{-3} and the surface area is approximately 50 m^2 g^{-1}. This is an incredibly large surface area per gram, on average about one fifth of a tennis court.

The TiO_2 powder contains a mixture of anatase and rutile in an approximately 4:1 proportion.

The mixture of anatase and rutile in these proportions is important to ensure the best photocatalytic properties of TiO_2 (see 'A new kind of water treatment').